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(54) Title: SUPPORTED METALLOCENE CATALYST FOR OLEFIN POLYMERIZATION

(57) Abstract

A highly active polyolefin catalyst can be prepared by reacting a reactive surface of a porous organic or inorganic support with a solution of metallocene compound dissolved in methylaluminoxane. One aspect of the invention is in a carrier which exhibits a silanol group concentration of greater than 0.7 mmole/gram. The catalyst is in particulate form with a particle size which exceeds 10 microns.

SUPPORTED METALLOCENE CATALYST
FOR OLEFIN POLYMERIZATION

This application is a continuation in part of Serial No. 141,911, filed October 2, 1993, and its refile under Rule 62 as Serial No. 08/494,654, filed June 26, 1995; said application is a continuation-in-part of applications Serial

5   Number 07/997,421, filed December 28, 1992, and Serial Number 08/036,786, filed March 25, 1993, each of which is relied upon and incorporated by reference herein.

The invention relates to improved catalysts and to modifications and improvements in polymerization and

10   copolymerization of ethylene, undertaken in the presence of catalysts comprising metallocenes of transition metals. The catalysts are characterized by extremely high activity. The catalysts of the invention operate smoothly in the gas phase, e.g. fluid bed. The catalysts produce high molecular weight

15   polymer at temperature and pressure conditions typically found in a commercial fluid bed reactor. Moreover, the catalyst yields high bulk density, granular linear low density polyethylene in slurry polymerizations without reactor fouling. The polymer products have narrow

20   molecular weight distribution, are free of gels, and, for linear low density have homogeneous comonomer distribution. Reactor fouling is eliminated in both gas phase fluid bed and slurry polymerizations.

Polyethylene is produced commercially in a gas phase

25   reaction in the absence of solvents by employing selected chromium and titanium-containing catalysts under specific operating conditions in a fluid bed process. Polyethylene products of those original processes exhibited medium-to-broad molecular weight distribution. To be commercially

30   useful in the gas phase fluid bed process, or slurry reactor process, undertaken at low pressures less than about 1000 psi, the catalyst must exhibit high activity, with concomitant high catalyst productivity, because these process

systems do not include catalyst residue removal procedures.
Accordingly, catalyst residue in the polymer product must be
so small that it can be left in the polymer without causing
any undue problems in the fabrication and/or to the ultimate
5   consumer. To this end, the patent literature is replete with
developments of new catalysts.

    The use of metallocene compounds of transition metals as
catalysts for polymerization and copolymerization of ethylene
is one of those developments. Metallocenes can be described
10   by the empirical formula $Cp_mMA_nB_p$. These compounds in
combination with methylalumoxane (MAO) have been used to
produce olefin polymers and copolymers, such as ethylene and
propylene homopolymers, ethylene-butene and ethylene-hexene
copolymers.

15   Aluminoxanes, e.g. methylalumoxane (MAO), have been
used as co-catalyst with metallocene catalysts. The class of
alumoxanes (used interchangeably hereinafter with
"aluminoxane") comprises oligomeric linear and/or cyclic
alkylalumoxanes represented by the formula:
20     $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and $(-$
$Al(R)-O-)_m$ for oligomeric cyclic alumoxane wherein n is 1-40,
preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8
alkyl group and preferably methyl. Methylalumoxane is
commonly produced by reacting trimethylaluminum with water or
25   with hydrated inorganic salts, such as $CuSO_4 5H_2O$ or
$Al_2(SO_4)_3 \cdot 5H_2O$. Methylalumoxane can be also generated in
situ in polymerization reactors by adding to them
trimethylaluminum and water or water-containing inorganic
salts. MAO is a mixture of oligomers with a very wide
30   distribution of molecular weights and usually with an average
molecular weight of about 900-1200. MAO is typically kept in
solution in toluene. While the MAO solutions remain liquid
at fluid bed reactor temperatures, the MAO itself is a solid
at room temperature.

35   The slow development of the metallocene catalysts has
been in part attributable to the aluminoxane (hereinafter

used interchangeably with "alumoxane") reagent used to
activate. It was discovered that extensive reactor fouling
results when MAO solutions are fed directly into the gas
phase reactor in large enough quantities to provide this
5   liquid contact with metallocene compound. The fouling occurs
because the MAO solution forms a liquid film on the interior
walls of the reactor. The catalyst is activated when it
comes into contact with this liquid film, and the activated
catalyst reacts with ethylene to form a polymer coating which
10   grows larger in size until the reactor is fouled. In
addition, since substantially all of the activation takes
place on the walls, the MAO is not uniformly distributed to
the catalyst particles. The resulting non-homogeneous
polymerization gives low catalyst activity and poor product
15   properties.
        The invention relates to a metallocene catalyst which
does not require an aluminoxane cofeed to the polymerization
reactor. Moreover, the catalyst of the invention exhibits
high activity and productivity, in the fluid bed gas phase
20   and slurry polymerization and copolymerization of olefins.
        The problems invoked by the use of an alumoxane,
methylalumoxane, in catalyst production are addressed by the
catalyst of the invention, comprising a carrier material
impregnated with alumoxane and derivatives thereof, formed in
25   stages comprising:
        (1) providing a silica, which has 0.4 mmoles to 2.5
mmoles, preferably greater than 0.7 mmole, of hydroxyl
groups, also referred herein as silanol groups, per gram of
silica; [the silica is porous and has a particle size of 1 to
30   250 microns, having pores which have an average diameter of
50 to 500 Angstroms and having a pore volume of 0.5 to 5.0
cc/g of carrier; and a surface area of m^2/g to 600 m^2/g;
        (2) providing a volume of a liquid medium comprising an
alumoxane and a solvent therefor, wherein the concentration
35   of alumoxane, expressed as Al (elemental) weight percent is 5
to 20; the solution further contains a metallocene which is

present in an amount, expressed as elemental metal, which
ranges from 0.01 to 2 weight percent; wherein the
methylalumoxane provides aluminum in an amount sufficient to
provide a ratio of Al to silica, i.e., Al/silica (wt/wt)
ranging from 0.05 to 0.40; the volume of liquid medium
comprises an aromatic hydrocarbon and an aliphatic or
alicydic hydrocarbon and the volume exceeds the total pore
volume of the silica support;

    (3) contacting the said solution with the carrier and
allowing the solution to impregnate the pores of the carrier,
having a pore volume of 0.5 to 5.0 cc/g; and

    (4) after said contacting, recovering a dry impregnated
carrier which is an activated catalyst, effective as a
catalyst absent an aluminoxane cofeed.

    Accordingly, the invention includes the foregoing,
activated catalysts, the polymerizations and
copolymerizations catalyzed thereby, and the product(s)
thereof.

Catalyst Composition

    The catalysts of the invention comprise a carrier, an
alumoxane and at least one metallocene.

    The process of the invention results in supported
catalysts of transition metals and aluminum, with very
uniform distribution of metals within catalyst particles and
among catalyst particles. NMR and FTIR characterization
indicates that the alumoxane component of the catalyst reacts
with silica hydroxyl groups; NMR reveals substantially
complete reaction, and consumption of, alumoxane; in
accordance with the invention, the alumoxane reacts with a
silica support.

    The catalyst is free-flowing and particulate in form
comprising dry powder particles having an average particle
size of from 1 micron to 250 microns, preferably from 4
microns to 150 microns. The catalysts which contain only one
transition metal in the form of a metallocene have an
activity expressed in kg polymer/g of transition metals. The

aluminoxane and metallocene loading on the carrier is such
that the amount of aluminum, (elemental basis) provided by
the aluminoxane, on the carrier ranges from 1 to 40 wt.%,
preferably from 5 to 30 wt.%, and most preferably from 5 to
5   15 wt.%. The optimum MAO loading is in the range of 3 to 15
mmoles per gram of silica carrier; if a silica carrier is
overloaded with MAO, the catalyst activity is lower and the
catalyst particles agglomerate with attendant problems of
feeding and resin agglomeration.
10   The amount of metallocene on the carrier ranges, on a
transition metal elemental basis, from 0.001 to 10 wt.%,
preferably from 0.05 to 0.4 wt.%. Accordingly the ratio of
Al:Zr (on an elemental basis) in the catalyst can range from
25 to 10,000, usually within the range of from 70 to 980 but
15   preferably from 70 to 350 and most preferably from 100 to
350.
          The carrier material is a solid, particulate, porous,
preferably inorganic material, such as an oxide of silicon
and/or of aluminum. In the most preferred embodiment, the
20   carrier is silica in the form of spherical particles, e.g.,
as obtained by a spray-drying process. The carrier material
is used in the form of a dry powder having an average
particle size of from 1 micron to 500 microns, preferably
from 1 micron to 250 microns, and most preferably 10 microns
25   to 150 microns average particle size. If necessary, the
final catalyst containing carrier material may be sieved to
insure elimination of large catalyst particles. Presently,
elimination of catalyst particles that have a particle size
of greater than 500 microns is envisaged; preferably,
30   elimination of particles of greater than 250 micron particle
size, and, most preferably, elimination of particles of
greater than 150 micron particle size is undertaken. Sieving
of the material is preferably undertaken after impregnation
of the carrier with the metallocene and the aluminoxane.
35   This is highly desirable in the embodiment of the invention,
in which the catalyst contains only one transition metal in

the form of a metallocene and which is used to form narrow
molecular weight LLDPE, to reduce and/or to eliminate gels in
the final polyolefin product and to eliminate reactor hot
spots, thereby to insure reactor continuity, particularly in
the gas phase fluid bed process. The surface area of the
carrier is at least 3 square meters per gram (m^2/gm),
preferably, 5 to 1200 square meters per gram (m2/gm) and most
preferably at least 50 m^2/gm up to 600 m^2/gm. The pore
volume of the carrier will range from 0.1 to 5 cm_3 /gm,
preferably from 0.5 to 3.5 cm_3 /gm. The carrier material
should be dry, that is, free of physically absorbed water.

Preferably, the carrier is silica, which contains [OH]
groups or other functional groups that contain active
hydrogen. The carrier material must have at least some
active hydroxyl [OH] groups to produce the catalyst
composition of this invention. The hydroxyl group
concentration will be at least 0.7 mmole/gram silica.
Preferably, the hydroxyl group concentration of the silica
will range from 1.6 to 2.5 mmoles/gram silica. This range is
favored by lower drying, dehydration and/or calcination
temperatures.

Alternatively, the silica surface can be modified, well
known to people familiar with the art, to provide active
functional group to react with alumoxane. The active
functional group could be from hydroxyl, alcohols, acids,
phenols, and silanols.

The silica hydroxyl (herein silanol, silica hydroxyl is
used interchangeably) groups are detectable by IR
spectroscopy. Quantitative determinations of the hydroxyl
concentration on silica are made by contacting a silica
sample with methyl magnesium bromide and measuring methane
evolution (by pressure determination).

Dehydration of silica material can be effected by
heating at 100°C to 600°C, preferably from 150°C to 300°C and
most preferably at 250°C.

By comparison, silica dehydrated at 600°C (for 16 hours) will have a surface hydroxyl concentration of 0.7 mmoles per gram (mmols/gm) of silica.   Silica dehydrated at 800°C will be a silica with 0.5 mmole of silica hydroxy per gram silica.

5   The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m²/gm; pore volume of 1.65 cm³/gm), and it is a material marketed under the tradenames of Davison 948, 952 or 955 by the Davison Chemical Division of W. R. Grace and Company. As purchased, the

10   silicas are not dehydrated and must be dehydrated prior to use.

The effect of increasing silica hydroxyl groups on the catalyst activity and productivity is a positive one. The catalyst synthesis of the catalyst of the invention

15   exhibiting highest activity dictates that the silica contain hydroxyl groups for contact with the solution containing aluminoxane and metallocene, described below. It was determined that reaction of the hydroxyl groups of the silica with scavengers, such as trialkylaluminum compounds, e.g.,

20   trimethylaluminum (TMA), reduced the activity of the catalyst produced thereby compared to a catalyst formed with a silica having hydroxyl groups unreacted with such a scavenger. Silicas containing higher hydroxyl numbers produce catalysts of higher activity than silicas of lower

25   hydroxyl numbers. The amount of hydroxyl groups, in mmoles/gram silica can be affected by the dehydration temperatures used to condition the silica. Specifically, the dehydration temperatures of 600°C reduce the amount of reactive hydroxyl groups to 0.7 mmole per gram of silica for

30   contact with the solution of aluminoxane and metallocene. By comparison, the dehydration temperatures of 250°C reduce the amount of reactive hydroxyl groups to 2 mmole per gram of silica for contact with the solution of aluminoxane and metallocene.   Accordingly, the silica used in embodiments of

35   the invention will contain a silanol (OH) concentration of greater than 0.4 mmoles OH per gram silica; preferably it

will contain greater than 0.7 mmoles to up to 2.5 mmoles OH
per gram of silica.   In preferred embodiments, the
concentration ranges from 1.6 to 2.5 mmoles/gram silica.

5
To form catalysts of the invention, all metallocene
components can be dissolved with alumoxane and impregnated
into the carrier. Catalyst preparation is undertaken under
anhydrous conditions and in the absence of oxygen. Metal
impregnation temperatures range from 0 to 60°C. Impregnation
is effected with agitation. Contact of the silica with the

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impregnant aluminoxane solution results in a reaction product
between the alumoxane and silica. The reaction can be
detected by NMR analysis. The reaction results in depletion
of any alumoxane in solution. In preferred embodiments, this
results in no free alumoxane in the resulting catalyst. The

15
resulting catalyst is characterized by very high transition
metal and aluminum efficiencies.

The class of alumoxanes comprises oligomeric linear
and/or cyclic alkylalumoxanes represented by the formula:
$R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and (-

20
$Al(R)-O-)_m$ for oligomeric cyclic alumoxane wherein n is 1-40,
preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8
alkyl group and preferably methyl. MAO is a mixture of
oligomers with a very wide distribution of molecular weights
and usually with an average molecular weight of 800 to 1200.

25
MAO is typically kept in solution in toluene.

The support, preferably a silica support, is impregnated
with a solution of alumoxane. The solution of alumoxane can
contain the metallocene compound(s), described below. The
solvent for the alumoxane is preferably toluene. However,

30
other hydrocarbon solvents may be used instead of the
toluene; illustrative of such hydrocarbons are those which
contain 5 to 20 carbon atoms, such as ethylbenzene, xylene,
cumene, cyclopentane, cyclohexane, cycloheptane, pentane,
isopentane, hexane, isohexane, heptane, octane, and decane or

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mixture thereof. The solvent for the alumoxane can be used
to form a solution with a volume which is equal to or less

than the pore volume of the silica. A critical aspect of the impregnation process is the use of a liquid medium in addition to the alumoxane solution. The liquid medium is a hydrocarbon which contains 5 to 20 carbon atoms; illustrative

5 compounds which can be used as the liquid medium include pentane, isopentane, hexane, isohexane, heptane, octane, nonane, decane, dodecane, cyclopentane, cyclohexane, and cycloheptane or mixture thereof. Isomers of these hydrocarbons could also be used.

10 The volume of the liquid medium is also critical in that this volume must be sufficient to form a slurry. In general this volume should be 2 to 15 times the pore volume of the support as measured by nitrogen adsorption method (BET method). For example, for a silica support with 1.5 cc/g

15 pore volume, a minimum of 3 cc of the second medium, e.g., hexane, and a maximum of 20 cc/g silica would be employed.

To obtain a uniform distribution of methylalumoxane and metallocene on silica, it is critical that during the reaction step between methylalumoxane, metallocene, and

20 silica are complete such that more than 99% of the methylalumoxane and metallocene have reacted with the silica surface or chemically adsorbed on the silica surface and negligible amount of methylalumoxane and metallocene remained in the liquid medium outside of the silica pores. Excess

25 amount of methylalumoxane and metallocene would require extra washing steps to remove these excesses or the methylalumoxane could cross linked or precipitated outside the silica pore forming a coating on the outside boundary of the silica resulting in non-uniform distribution of methylalumoxane and

30 metallocene. Non-uniform distribution of methylalumoxane and metallocene catalyst not supported on silica surface, eventually can cause reactor fouling problems both in slurry reactor and in gas phase reactor.

The use of the liquid medium results in uniform

35 dispersion of the metals on the surface and pores of the catalyst support. Use of the liquid medium improves aluminum

distribution, reduces catalyst agglomeration and, indirectly
or directly, increases continuity. The uniform distribution
of aluminum is revealed in electron micrographs of the
catalysts. Saturated hydrocarbon liquid was found to be a
5   very effective medium to disperse silica, methylalumoxane in
toluene, and metallocene to give a supported catalyst with
very uniform distribution of metals within catalyst particles
and among catalyst particles. The final catalyst was
characterized by scanning electron microscope FTIR, and solid
10   state NMR. The methylalumoxane, it was found, reacted with
the silica hydroxyl group to form methylalumoxane silicate
with essentially no free methyl-alumoxane left in the final
catalyst as shown by FTIR and solid state NMR. We also found
the aluminum distribution within the particle and among the
15   particles are very uniformly distributed as measured by the
Al/Si ration on the surface of the silica particle and across
cross-sections of silica particles.

A common method to detect the distribution of various
chemical elements, such as silicon, aluminum, carbon, oxygen,
20   and zirconium, in particles less than 500 microscon in size
is the use of electron scanning microscopy. The description
of the use of a scanning electron microscope is specified in
the example section. In effect the catalyst particle are
observed under magnification. The existence of various
25   elements is detected by the energy dispersive spectrometer
equipped on the scanning electron microscope. The
distribution of each selected element can be displaced on a
photograph. Judging from the variation in the intensity of
each element among various particles, one can qualitatively
30   determine the distribution of each element on each silica
particle. To further quantify these observations, one can
randomly select a sample of catalyst particles (for example,
25 particles) in the microscope and measure the aluminum and
silicon signal for each silica particle. By dividing the
35   aluminum by silicon signal, some of the variation in due
sample angle and sample distance from the detector are

canceled resulting in an aluminum to silicon signal ratio
that can be correlated to the amount of aluminum reside
inside the silica pore. In our examples, for each catalyst
sample prepared, 25 Al/Si ratios were determined for each of
5   the 25 randomly selected particles. Standard statistical
calculation (reference: Box, G.E.P., et al. Statistics for
Experimenters, Wey: New York, 1978; p. 40) will give an
average Al/Si ratio and a standard deviation. Smaller
standard deviation represents more uniform Al/Si ratio from
10   one particle to another particle, and therefore more uniform
distribution of the aluminum or silica. Larger standard
deviation represent more variation in the Al/Si signal ratio
from one particle to another particle, and therefore less
uniform distribution of the aluminum. In our examples, it
15   was shown that by using the method of reaction of silica with
methylalumoxane and metallocene, the catalyst particles were
found to have Al/Si signal ratio that have relatively small
standard deviation of less than 25% of the average. Due to
variation in reactor configuration, reactor size, flow rate
20   of the reagents and the agitator speed, and also due to
normal variation in the scanning electron microscope, the
standard deviation could be as high as 50%.

Similarly, the Al/Si signal ratio can be determined for
a cross-section of a catalyst particle. The catalyst
25   particles were first sectioned, and 10 cross-sectioned
particles were randomly chosen. The Al and Si signal were
obtained for the center of each particle and the edge
(defined as the 2 micron layer just underneath the outmost
boundary of a catalyst particle) of each particle.
30   Comparison of the average Al/Si signal ratio for (a) the
surfaces of the catalyst particles, (b) the centers of the
cross-sections of the catalyst particles, and (c) the edges
of the cross-sections of the catalyst particles would
indicate the uniform distribution of aluminum within the
35   catalyst particles. In general, the difference among the
Al/Si signal ratios from (a), (b) and (c) should not be more

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than 30% more each other and preferably less than 15% from
each other.

Accordingly and preferably, the maximum volume of the
alumoxane solution is the total pore volume of the carrier

5   material sample. That maximum volume of the alumoxane
solution insures that the solvent used in the alumoxane
solution does not demonstrate or change the properties of the
liquid medium chosen to disperse the silica. By way of
example, if the pore volume of the carrier material is 1.65

10   cc/gm, then the volume of alumoxane will be equal to or less
than 1.65 cc/gm of carrier material. Thus, the maximum
volume of solution (of metallocene and alumoxane) will equal
the total pore volume of the carrier, e.g. silica, which is
the pore volume in, e.g., cc/gm, times the total weight of

15   the carrier used.

The solvent or the hydrocarbon liquid may be removed
from the pores of the carrier material by heating and/or
under a vacuum or purged with heating in an inert gas, such
as nitrogen. The hydrocarbon liquid can also be removed by

20   filtering or decanting. If elevated temperature is employed,
the temperature conditions in this step are controlled to
reduce, if not to eliminate, agglomeration of impregnated
carrier particles and/or crosslinking of the alumoxane. In
this step, solvent can be removed by evaporation effected at

25   relatively low elevated temperatures of above 40° and below
50° to obviate agglomeration of catalyst particles and
crosslinking of the alumoxane. Preferably drying is
undertaken at 45°C or less for 5 to 7 hours. Although solvent
can be removed by evaporation at relatively higher

30   temperatures than that defined by the range above 40° and
below 50°C, very short heating times schedules must be
employed to obviate agglomeration of catalyst particles and
crosslinking of the alumoxane, with reduction of catalyst
activity. Accordingly, an active catalyst has been produced

35   at drying temperature of 110°C at extremely short heating

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times, whereas at 45°C, drying can be undertaken for periods
of several days.

In a preferred embodiment, the metallocene is added to
the solution of the alumoxane prior to impregnating the
5   carrier with the solution. The mole ratio of aluminum
provided by aluminoxane, expressed as Al, to metallocene
metal expressed as M (e.g. Zr), ranges from 25 to 10,000,
preferably 75 to 980, and most preferably 100 to 350. An
added advantage of the present invention is that this Al:Zr
10   ratio can be directly controlled. In a preferred embodiment
the alumoxane and metallocene compound are mixed together at
ambient temperature for 0.1 to 24 hours, prior to use in the
impregnated step. The solvent for the metallocene and
alumoxane can be appropriate hydrocarbon solvents, such as
15   toluene, xylene, ethyl benzene, cumean, pentane, isopentane,
hexane, isohexane, heptane, and octane, or mixtures thereof,
preferably it is toluene. In addition to the alumoxane
solvent the silica impregnant medium comprises an aliphatic
or alicyclic diluent. The invention further comprises a
20   process for preparing a catalyst for the polymerization
and/or copolymerization of ethylene and/or alpha-olefins of 3
to 10 carbon atoms and for producing products exhibiting a
bulk density of 15 to 36 lb/ft3. [Some of the products are
characterized by MFR of 14 to 25 (wherein said MFR is the
25   ratio I21/I2 wherein I21 is measured at 190°C in accordance
with ASTM D-1238, Condition F and I 2 is in accordance with
ASTM D-1238, Condition E),] wherein the catalyst is in the
form of particles, wherein said particles have an average
particle size in the range of 1 to 500 microns; wherein said
30   particles comprise silica, a transition metal and aluminum,
wherein the ratio of aluminum to transition metal ranges from
70 to 350; wherein the process comprises providing an
amorphous porous hydrated silica and dehydrating said silica
at a dehydration temperature of less than 300°C to provide a
35   dehydrated silica having a silanol concentration of at least
0.7 millimoles per gram silica, wherein said dehydrated

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silica is further characterized by a pore volume in the range
of 0.1 to 5 cc/gm; providing a volume of a mixture of a
metallocene and an aluminoxane, wherein said volume of said
mixture is equal to or less than the total pore volume of
5   said dehydrated silica, wherein said metallocene has a
formula, $Cp_mMA_nB_p$, wherein Cp is a cyclopentadienyl or a
substituted cyclopentadienyl group; m is 1 or 2; M is
zirconium or hafnium; and each of A and B is selected from
the group consisting of a halogen atom, a hydrogen atom and
10   an alkyl group, providing that m+n+p is equal to the valence
of the metal M; wherein said alumoxane has a formula (a) or
(b); wherein (a) is $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear
alumoxanes and (b) is $(-Al(R)-O-)_m$ for oligomeric cyclic
alumoxane wherein n is 1-40, m is 3-40, and R is a C_1-C_8 alkyl
15   group; contacting said silica with said volume of said
mixture, to allow impregnation of the pores of said silica
with said mixture; and recovering an activated catalyst; the
volume of the mixture of the metallocene and alumoxane is
admixed with a second liquid medium, defined above, which is
20   a dispersant for the transition metal and alumoxane.

        The metallocene compound has the formula $Cp_mMA_nB_p$ in
which Cp is an unsubstituted or substituted cyclopentadienyl
group, M is zirconium or hafnium and A and B belong to the
group including a halogen atom, hydrogen or an alkyl group.
25   In the above formula of the metallocene compound, the
preferred transition metal atom M is zirconium. In the above
formula of the metallocene compound, the Cp group is an,
unsubstituted, a mono- or a polysubstituted cyclopenta-dienyl
group. The substituents on the cyclopentadienyl group can be
30   preferably straight-or branched chain C_1-C_6 alkyl groups. The
cyclopentadienyl group can be also a part of a bicyclic or a
tricyclic moiety such as indenyl, tetrahydroindenyl,
fluorenyl or a partially hydrogenated fluorenyl group, as
well as a part of a substituted bicyclic or tricyclic moiety.
35   In the case when m in the above formula of the metallocene
compound is equal to 2, the cyclopentadienyl groups can be

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also bridged by polymethylene or dialkylsilane groups, such
as $-CH_2-$, $-CH_2-CH_2-$, $-CR'R''-$ and $-CR'R''-CR'R''-$ where R' and R"
are short alkyl groups or hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-$
$CH_2-Si(CH_3)_2-$ and similar bridge groups. If the A and B

5   substituents in the above formula of the metallocene compound
are halogen atoms, they belong to the group of fluorine,
chlorine, bromine or iodine. If the substituents A and B in
the above formula of the metallocene compound are alkyl
groups, they are preferably straight-chain or branched C_1-C_8

10   alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-
butyl, isobutyl, n-pentyl, n-hexyl or n-octyl or phenyl,
benzyl, substituted phenyl, or substituted benzyl groups. If
the substituents A and B in the above formula of the
metallocene compounds are aryl groups, they are preferably

15   phenyl or benzyl groups or derivatives of these groups.
       Suitable metallocene compounds include:
bis(cyclopentadienyl)metal dihalides,
bis(cyclopentadienyl)metal hydridohalides,
bis(cyclopentadienyl)metal monoalkyl monohalides,

20   bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal
dihalides wherein the metal is zirconium or hafnium, halide
groups are preferably chlorine and the alkyl groups are C_1-C_6
alkyls. Illustrative, but non-limiting examples of
metallocenes include bis(cyclopentadienyl)zirconium

25   dichloride, bis(cyclopentadienyl)hafnium dichloride,
bis(cyclopentadienyl)zirconium dimethyl,
bis(cyclopentadienyl)hafnium dimethyl,
bis(cyclopentadienyl)zirconium hydridochloride,
bis(cyclopentadienyl)hafnium hydridochloride, bis(n-

30   butylcyclopentadienyl)zirconium dichloride, bis(n-
butylcyclopentadienyl)hafnium dichloride, bis(n-
butylcyclopentadienyl)zirconium dimethyl, bis(n-
butylcyclopentadienyl)hafnium dimethyl, bis(n-
butylcyclopentadienyl)zirconium hydridochloride, bis(n-

35   butylcyclopentadienyl)hafnium hydridochloride,
bis(pentamethylcyclopentadienyl)zirconium dichloride,

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bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-
butylcyclopentadienyl)zirconium dichloride, bis-(1,3-
dimethylcyclopentadienyl)zirconium dichloride,
bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-
5   indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-
tetrahydro-1-indenyl)] zirconium dichloride. The metallocene
compounds utilized within the embodiment of this art can be
used as crystalline solids, as solutions in aromatic
hydrocarbons or in a supported form.
10   These catalysts are effective to run at low pressures,
up to, specifically no greater than, 1000 psi, at
temperatures up to 130°C. These catalysts exhibit long
catalyst life, high activity and productivity, and produce
high bulk density products.

15   Conditions for the polymerization and copolymerization of
       ethylene
          The process of the invention may be undertaken in gas
phase, in fluid bed gas phase, or in slurry. The catalyst of
the invention exhibits long catalyst life. The catalyst of
20   the invention, allows for the production of linear low
density polyethylene in the gas phase or in a slurry
polymerization without reactor fouling. With respect to the
slurry operation to produce LLDPE, particulate linear low
density polyethylene is produced in the slurry reactor and is
25   not swollen (by the solvent). The products from both the gas
phase (e.g. fluid bed) and slurry have a high bulk density,
which allows for increased throughput of product per weight
of catalyst.
          Preferably, the polymerization (copolymerization) is
30   undertaken at a temperature and/or pressure below the
sintering temperature of the polymer particles. Most
preferably, the process is undertaken in the fluid bed gas
phase or in a slurry reactor. The high activity of the
catalysts herein allow for efficacious low pressure fluid bed
35   gas phase and/or slurry process product production. Much

lower activity catalysts than those described herein may be
employed in high pressure processes at pressures which exceed
400 psi, such as solution and high pressure slurry
polymerizations. For the production of ethylene copolymers

5   in the process of the present invention an operating
temperature of 30° to 115°C is preferred, and a temperature of
70° to 106°C is most preferred. Temperatures of 75° to 90°C
are used to prepare products having a density of 0.91 to
0.92, and temperatures of 80° to 100°C are used to prepare

10 products having a density of 0.92 to 0.94, and temperatures
of 90° to 115°C are used to prepare products having a density
of 0.94 to 0.96.

In the gas phase, linear low density production is
conducted at 85°C and high density product is formed at 105°C.

15 In slurry polymerization, linear low density production is
conducted at 70°C and high density production is conducted at
90°C.

In polymerizations described herein, pressures are below
10000 psi, preferably below 1000 psi. The fluid bed reactor

20 is operated at pressures of up to 1000 psi, and is preferably
operated at a pressure of from 150 to 500 psi, with operation
at the higher pressures in such ranges favoring heat transfer
since an increase in pressure increases the unit volume heat
capacity of the gas.

25 The partially or completely activated catalyst is
injected into the bed at a point above the distribution plate
at a rate equal to its consumption. Since the catalysts used
in the practice of this invention are highly active,
injection of the fully activated catalyst into the area below

30 the distribution plate may cause polymerization to begin
there and eventually cause plugging of the distribution
plate. Injection into the bed, instead, aids in distributing
the catalyst throughout the bed and precludes the formation
of localized spots of high catalyst concentration.

35 The production rate of polymer in the bed is controlled
by the rate of catalyst injection. Since any change in the

rate of catalyst injection changes the rate of generation of
the heat of reaction, the temperature of the recycle gas is
adjusted to accommodate the change in rate of heat
generation. Complete instrumentation of both the fluidized

5   bed and the recycle gas cooling system is, of course,
necessary to detect any temperature change in the bed so as
to enable the operator to make a suitable adjustment in the
temperature of the recycle gas.

Since the rate of heat generation is directly related to

10 product formation, a measurement of the temperature rise of
the gas across the reactor (the difference between inlet gas
temperature and exit gas temperature) is determinative of the
rate of particulate polymer formation at a constant gas
velocity.

15 The polymerization and copolymerization products

Both low density (0.91 to 0.939 g./cc) and high density
(0.94 to 0.965 and above) products with high bulk density,
low (hexane) extractables and granular morphology can be
prepared in the slurry or gas phase reactor with no fouling.

20 The resin produced has a high molecular weight, narrow
molecular weight distribution, and homogeneous branching
distribution. The catalyst ash contains small amounts of Zr
and Al, e.g., less than 1 ppm Zr and 50 ppm Al. The high
activity of the catalysts of the invention which also exhibit

25 long catalyst life and produce high bulk density products are
significant factors in the unexpected efficacy of these
catalysts in catalytic polymerizations and copolymerizations
of olefins.

Ethylene polymers, as well as copolymers of ethylene

30 with one or more C_3-C_{10} alpha-olefins, can be produced in
accordance with the invention. Thus, copolymers having two
monomeric units are possible as well as terpolymers having
three monomeric units. Particular examples of such polymers
include ethylene/1-butene copolymers, ethylene/1-hexene

35 copolymers and ethylene/4-methyl-1-pentene copolymers.

Since the catalyst is effective to incorporate comonomer
in a regular manner the resin may contain blocks of
polymerized product of alpha olefins of 3 to 10 carbon atoms
in the resin backbone. These blocks will consist essentially
5   of dimers, oligomers, polymers and admixtures thereof.
Because of the excellent comonomer incorporation of the
catalyst and the branching homogeneity of the resin,
significant amount of hexene saving can be achieved.

Ethylene/1-butene and ethylene/1-hexene copolymers are
10 the most preferred copolymers polymerized in the process of
and with the catalyst of this invention. The ethylene
copolymers produced in accordance with the present invention
preferably contain at least about 80% by weight of ethylene
units. The cocatalyst of this invention can also be used
15 with the catalyst precursor of this invention to polymerize
propylene and other alpha-olefins and to copolymerize them.
The structure of alpha-olefin polymers prepared with the
cocatalyst and the catalyst precursor of this invention
depends on the structure of the cyclopentadienyl ligands
20 attached to the metal atom in the catalyst precursor
molecule. The cocatalyst compositions of this invention can
also be used with the catalyst precursors of this invention
to polymerize cycloolefins such as cyclopentene.

Hydrogen may be used as a chain transfer agent in the
25 polymerization reaction of the present invention. The ratio
of hydrogen/ethylene employed will vary between 0 to 2.0
moles of hydrogen per mole of ethylene in the gas phase. Any
gas inert to the catalyst and reactants can also be present
in the gas stream.

30 In one embodiment, the catalyst of the invention
exhibits high activity for polymerization of ethylene and
higher alpha-olefins and allows the synthesis of ethylene
polymers and copolymers with a relatively narrow molecular
weight distribution and homogeneous branching distribution.
35 The molecular weight distribution is determined as MFR which
ranges from 15 to 25, in polymerizations of the invention.

Branching distribution in ethylene copolymers is evaluated on the basis of the resin's melting point. Relatively homogeneous branching distribution is one which the melting point ranges from 100° to 120°C, depending on comonomer

5   composition. In this embodiment, the catalyst of the invention contains only one source of transition metal, a metallocene.

Particularly, the copolymer products contain 0.1 to 2 ppm of Zr. The product has an average particle size of

10 0.015-0.035 inches, settled bulk density from 20 to 36 lb/ft3. The particles of product are spherical. The narrow molecular weight distribution low density copolymers have been produced with MI of one (1) and less than 1, down to 0.01. The low density products of the invention exhibit a MI

15 which can range from 0.01 to 5, preferably from 0.5 to 4, and most preferably 0.8 to 2.0. The low density products of the invention exhibit a melt flow ratio (MFR) of 14 to 25 preferably from 14 to 20; products with MFR ranging from 16 to 18 have been made; MFR is the ratio I 21/I2 [wherein I21

20 is measured at 190°C in accordance with ASTM D-1238, Condition F, and I2 is measured in accordance with ASTM D-1238, Condition E]. When fabricated into films, the films of the copolymers exhibit balanced tear strength, as measured by ASTM D-1922. Furthermore the LLDPE of the invention exhibits

25 Dart Drop Impact values as measured by ASTM D-1709 of greater than 800. The products of the catalysis with the catalyst of the invention can be used as films which are substantially free of gels. The films exhibit very low haze values as measured by ASTM D-1003, preferably in the range of 3 to 10,

30 more preferably from 5 to 7.

EXAMPLES

Catalyst Preparation

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Example 1

Davison 955 silica was dehydrated at 250°C.   10.0 grams
of this dehydrated silica were added to a 300 ml flask; and
50 cc of heptane were added to the silica to form a slurry
5   mixture.   In a separate bottle, 0.142 grams of bis(n-
butylcyclopentadienyl) zirconium dichloride was dissolved in
13.41 grams of a 30 wt.% methyalumoxane solution in toluene.
This solution was added slowly to the silica over a period of
30 minutes.   The slurry mixture was then dried at 45°C with
10   nitrogen purge for 16 hours.   13.7 grams of free flowing
catalyst were obtained and analyzed to contain 13.2 wt.% Al
and 0.23 wt.% Zr.

Example 2 (comparative example)

The same procedures was used as in example 1 except no
15   silica was used.   3.235 grams of solid were collected and
analyzed to contain 32.8 wt.% Al and 0.65 wt.% Zr.

Example 3

Davison 955 silica was dehydrated at 250°C.   20.07 grams
of this dehydrated silica were added to a 500 ml flask with
20   an addition funnel and equipped with a pedal stirrer.   100 cc
isohexane were added through the addition funnel into the
silica to form a slurry mixture.   In a separate bottle, 0.284
grams of bis(n-butylcyclopentadienyl) zirconium dichloride
was dissolved in 32.08 cc of a 30 wt.% methyalumoxane
25   solution in toluene.   This solution was added slowly over a
period of 30 minutes.   The slurry was mixed thoroughly, and
20 cc of the clear solvent were decanted from the slurry for
analysis of Al and Zr.   The slurry mixture was then dried at
45°C with nitrogen purge for 16 hours.   27.8 grams of free
30   flowing catalyst were collected and analyzed to contain 12.0
wt.% Al and 0.22 wt.% Zr.

Analysis of the 20 cc solvent decanted from the slurry
mixture was shown to contain 3.30 mg of Al and 0.060 mg of
Zr.   Calculation showed that 99.4% of the total Al from the
35   MAO reacted with the silica, and only 0.56% of the total Al
from MAO remained in the solvent.   Similarly, 99.4% of the

total Zr from metallocene was in the silica and 0.60% of the
total Zr from metallocene remained in the solvent phase.
Example 4

Davison 955 silica was dehydrated at 250°C. 20.162
5   grams of this dehydrated silica were added to a 500 ml flask
equipped with an addition funnel and a pedal stirrer. 100 cc
isohexane and 0.5 cc of 15 wt.% trimethylaluminum in heptane
were added into the addition funnel. This solution was then
added to the silica to form a slurry mixture. In a separate
10   bottle, 0.473 grams bis(n-butylcyclopentadienyl) zirconium
dichloride was dissolved in 32.2 cc of a 30 wt.%
methyalumoxane solution in toluene. This solution was then
added slowly over a period of 30 minutes. The slurry was
mixed thoroughly for 30 minutes and 20 cc of the clear
15   solvent was decanted from the slurry for Al and Zr analysis.
The slurry mixture was then dried at 45°C with nitrogen purge
for 16 hours. 27.412 grams of free flowing catalyst were
collected and analyzed to contain 11.8 wt.% Al and 0.35 wt.%
Zr.
20   Analysis of the 20 cc solvent decanted from the slurry
mixture was shown to contain 0.53 mg of Al and 0.014 mg of
Zr. Calculation showed that 99.9% of the total Al from the
MAO reacted with the silica and 0.09% of the total Al from
MAO remained in the solvent. Similarly, 99.9% of the total
25   Zr from metallocene were inside the silica pore and 0.09% of
the total Zr from metallocene remained in the solvent phase.
Example 5   (Comparative example)

Davison 955 silica was dehydrated at 600°C. 15.63 grams
of this dehydrated silica were added to a 500 ml flask
30   equipped with an addition funnel and a pedal stirrer. 75 cc
isohexane and 0.4 cc of 15 wt.% trimethylaluminum in heptane
were added into the addition funnel. This solution was then
added to the silica to form a slurry mixture. In a separate
bottle, 0.367 grams bis(n-butylcyclopentadienyl) zirconium
35   dichloride was dissolved in 22.74 cc of a 30 wt.% methy-
alumoxane solution in toluene. This solution was then added

slowly over a period of 30 minutes. The slurry was mixed
thoroughly for 30 minutes and 15 cc of solvent were then
decanted from the slurry for Al and Zr analysis. The solvent
phase was cloudy and white in color, indicative of excessive
5   amount of methylalumoxane that did not react with the silica.
The slurry mixture was then dried at 45°C with nitrogen purge
for 16 hours. 20.5 grams of free flowing powder was
collected and analyzed to contain 11.4 wt.% Al and 0.32 wt.%
Zr. Analysis of the 15 cc solvent decanted from the slurry
10   mixture was shown to contain 41.2 mg of Al and 1.27 mg of Zr.
Calculation showed that 90.7% of the total Al from the MAO
reacted with the silica and 9.29% of the total Al from MAO
remained in the solvent. Similarly, 89.8% of the total Zr
from metallocene were inside the silica pore and 10.23% of
15   the total Zr from metallocene remained in the solvent phase.
Example 6
    Davison 955 silica was dehydrated at 600°C. 20.06 grams
of this dehydrated silica were added to a 500 ml flask with
an addition funnel and a pedal stirrer attached. 100 cc
20   isohexane and 0.5cc of 15 wt.% trimethylaluminum in heptane
were added to the addition funnel. This solution was then
added to the silica to form a slurry mixture. In a separate
bottle, 0.325 grams bis(n-butylcyclopentadienyl) zirconium
dichloride was dissolved in 20.84 cc of a 30 wt.% methy-
25   alumoxane solution in toluene and additional 7 cc of toluene
were added. This solution was then added slowly over a
period of 30 minutes to the silica. The slurry was then
thoroughly mixed for 30 minutes and 20 cc of solvent were
then decanted from the slurry for Al and Zr analysis. The
30   slurry mixture was then dried at 45°C with nitrogen purge for
16 hours.   26.0 grams of free flowing powder were collected
and analyzed to contain 9.51 wt.% Al and 0.27 wt.% Zr.
    Analysis of the 20 cc solvent decanted from the slurry
mixture was shown to contain 1.62 mg of Al and 0.024 mg of
35   Zr. Calculation showed that 99.6% of the total Al from the
MAO reacted with the silica and 0.37% of the total Al from

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MAO remained in the solvent. Similarly, 99.8% of the total
Zr from metallocene were inside the silica pore and 0.20% of
the total Zr from metallocene remained in the solvent phase.
Example 7

5   Same procedure was used as example 6 except that 16.1 cc
of 30 wt% methyalumoxane and 0.236 gram of bis(n-
butylcyclopentadienyl) zirconium dichloride was used. 23.985
grams of a free flowing powder catalyst were collected and
analyzed to contain 7.36 wt.% Al and 0.22 wt.% Zr.

10   Analysis of the 20 cc solvent decanted from the slurry
mixture was shown to contain 0.13 mg of Al and 0.0037 mg of
Zr. Calculation showed that 99.96% of the total Al from the
MAO reacted with the silica and 0.04% of the total Al from
MAO remained in the solvent. Similarly, 99.9% of the total

15   Zr from metallocene were inside the silica pore and 0.04% of
the total Zr from metallocene remained in the solvent phase.
Example 8
          Silica was dehydrated at 250°C. 5.00 grams of this
silica were added to a 100 ml Schlenk flask equipped with a

20   magnetic stirrer. 25 cc of isohexane were transferred into
the flask to form a slurry mixture. This slurry mixture was
chilled in an ice bath at 0°C. In a separate bottle, 0.047
grams of bis(n-butylcyclopentadienyl) zirconium dichloride
was dissolved in 7.7 cc of 30 wt.% methylalumoxane in

25   toluene. This solution was then transferred slowly into the
silica slurry over a period of 5 minutes while stirring
vigorously. The slurry mixture was then dried at 45°C with
nitrogen purge for 4 hours. 6.3 grams of free flowing
catalyst were obtained and analyzed to contain 11.9 wt.% Al

30   and 0.15 wt.% Zr.
Example 9
          Silica was dehydrated at 250°C. 5.0 gram of this silica
were added to a 100 ml Schlenk flask equipped with a magnetic
stirrer. 25 cc of isohexane were transferred into the flask

35   to form a slurry mixture. In a separate bottle, 0.047 grams
of bis(n-butylcyclopentadienyl) zirconium dichloride was

dissolved in 5.5 cc of 30 wt.% methylalumoxane in toluene.
This solution was then transferred slowly into the silica
slurry over a period of 10 minutes with vigorous stirring.
The slurry mixture was then dried at 45°C with nitrogen purge
5   for 4 hours. 6.4 grams of free flowing dry catalyst were
collected and analyzed to contain 10.3 wt.% Al and 0.16 wt.%
Zr.

Example 10

        Silica was dehydrated at 600°C. 5.0 grams of this
10   silica were weighed into a 100 ml Schlenk flask equipped with
a magnetic stirrer. 25 cc of isohexane were transferred into
the flask to form a slurry mixture. In a separate bottle,
0.047 gram of bis(n-butylcyclopentadienyl) zirconium
dichloride was dissolved in 5.5 cc of 30 wt.%
15   methylaluminoxane in toluene and additional 1.9 cc of toluene
was added. This solution was then transferred slowly into
the silica slurry over a period of 10 minutes with vigorous
stirring. The slurry mixture was then stirred for an
additional 30 minutes before the clear solvent layer was
20   decanted off. The remaining mixture was then dried at 45°C
with nitrogen purge for 16 hours. 6.3 grams of free flowing
dry catalyst were obtained and analyzed to contain 10.4 wt.%
Al and 0.18 wt.% Zr.

Polymerization Results

25   Polymerization was conducted in a 2.5 liter autoclave
which was free from air and moisture by purging with nitrogen
at 120°C. The autoclave was cooled to 25°C and 1 liter of
polymerization grade heptane, 100 cc hexene, 2 cc
triisobutylaluminum (25 wt.% in heptane) were added to the
30   reactor. The reactor temperature was then equilibrated at
70°C with ethylene at 128 psig total pressure. About 100 mg
of a catalyst from Example 1 to 8 were used in the reactor.
Polymerization started immediately and was allowed to
continue for about 60 minutes before polymerization was
35   stopped by injection of methanol. The solvent was removed

and polymer was dried in a vacuum oven at 60°C.   Results are
summarized in Table 1:

Table 1

	Catalyst	Productivity g/g-cat/hr	Al efficiency kg/g-Al/hr	Zr efficiency kg/g-Zr/hr	I2	I21	MFR	Density g/cc	Hexene mole %
5	1	2500	18.8	1100	3.4	67.6	19.6	0.922	1.9
	2	3800	11.6	600	1.4	29.6	20.6	0.917	2.3
	3	2700	22.2	1200	2.6	44.3	20.6	0.920	2.5
	4	4000	33.7	1100	2.8	57.0	20.2	0.922	1.9
	5	3600	31.9	1100	1.2	28.7	24.5	0.920	2.3
10	6	2500	26.7	900	2.7	54.9	20.5	0.917	2.4
	7	1700	23.2	800	3.3	72.0	21.7	0.924	2.1
	8	2700	22.7	1800	2.5	51.8	20.8	0.919	2.3
	9	2400	23.1	1500	3.0	64.3	21.4	0.922	2.1
	10	2500	24.1	1400	2.9	61.1	21.1	0.922	2.0

15   In all examples above, free flowing granular resin was
obtained with high bulk density of more than 0.30 g/cc except
for the two comparative examples (example 2 and 5).   In both
cases of example 2 and 5, reactor fouling was observed.
Reactor temperature control was poor or the ethylene feed
20   line was plugged leading to early shut down of reactor.   When
the reactor was opened, large amount of resin sheet(s) and
chunks were found on reactor wall, agitator, and
thermocouple.

Uniform Distribution of Methylalumoxane on Support

25   The following examples illustrate the uniform
distribution of aluminum (from methylalumoxane) among silica
particles and within each silica particles:

Example 11

        Davison 955 silica was dehydrated at 250°C.   655 grams of
30   this dehydrated silica were added to a two-gallon mix-vessel;
and 3280 cc of isopentane were added to the silica to form a
slurry mixture.   In a separate step, 6.174 grams of bis(n-
butylcyclopentadienyl) zirconium dichloride were dissolved in
923 grams of a 30 wt.% methylalumoxane solution in toluene.

27

This solution was then pumped slowly at 12.0 cc/minute to the slurry mixture which was agitated at 120 rpm. After the addition, the slurry was allowed to mixed for 14 minutes and was then dried at 45°C with nitrogen purge for 15 hours.

5   886 grams of free flowing catalyst were obtained and analyzed to contain 12.7 wt.% Al and 0.15 wt.% Zr.

Example 12

Same as Example 11, except that 664 grams of silica, 3325 cc of isopentane, 934 grams of methylalumoxane, and 6.250

10   grams of bis(n- butylcyclopentadienyl) were used. 829 grams of free flowing catalyst were obtained and analyzed to contain 12.5 wt.% Al and 0.15 wt.% Zr.

Example 13

Same as Example 11, except that 658 grams of silica, 3290

15   cc of isopentane, 923.4 grams of methylalumoxane, and 6.200 grams of bis(n- butylcyclopentadienyl) were used. 912 grams of free flowing catalyst were obtained and analyzed to contain 12.2 wt.% Al and 0.14 wt.% Zr.

Microscopy Analysis

20   These catalysts were examined carefully using the microscopy method described below:

1. Equipment and Analysis:

Equipment Settings

The catalysts were analyzed with a JEOL JSM-840A SEM

25   equipped with a PGT OMEGA EDS detector. EDS scans and maps were collected on a SUN Sparcstation and processed with PGT X-Ray and Imaging Microanalysis Systems (IMIX) software. The EDS detection limit is 0.05-1.0 wt.% in a $1-8m^3$ volume, depending on the matrix. The gold peaks in the spectra are

30   from the conductive coating applied using a SPI-MODULE sputter coater to prevent charge buildup during the analysis.

All 12.8K pixel particle maps were collected at a 39mm. working distance (WD), 20KV accelerating voltage, 6m amp probe current, from secondary electron images (SEI) at 300X

35   magnification (sections were collected at 500X) with the objective aperture set at the 2 position. A filter assigns

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brightness levels to each pixel which correlate with the
relative selected element counts (the highest concentration
appears brightest while black indicates the absence of the
element). Use of the Al/Si ratio eliminates topographical
5   interference.

        EDS Small area particle scans (1-20 m^2) were collected at
2000-4000X. Cross-sectioned particle scans were collected at
the core and at the edge.

Surface Analysis of Aluminum and Silicon Elemental
10 Distribution

        Catalyst sample was mixed well and homogenized by
agitation. A representative sample was taken by a small
spatula. The catalyst powder was distributed on a 3 cm^2 area
of double-sided tape attached to a carbon disk. This sample
15 was then coated with gold using a SPI-MODULE^{tm} sputter coater.
The disk was placed into a JEOL SEM specimen holder and
viewed under the conditions specified for the JEOL JSM 840A
SEM. An area containing at least 25 particles at 300X
magnification was selected and imaged in the secondary
20 electron image (SEI) mode. 25 particles from this image were
randomly chosen and were labeled from 1 to 25 on the
photograph. An EDS (energy dispersive spectrometer) spectrum
was acquired using an OMEGA (or PRISM loaner) lithium-drifted
silicon crystal (Si(Li)) ultra-thin window detector at 6namps
25 probe current using PGT (Princeton Gamma-Tech) IMIX software
(version 8). Windows for aluminum, silicon, and oxygen were
selected. Image collection was selected from the root menu;
x-ray maps (map size 12800 or 25600 pixels) were collected
from the selected area and printed on a Mitsubishi CP210U
30 color video processor. X-ray analysis/x-ray collect was
selected from the root menu. A spectrum was acquired with
the conditions set at 10 seconds, 6nA, 20kV accelerating
voltage, 30° take-off angle from the a 4 m^2 small area scan of
each numbered particle at 4,000X. From the image menu,
35 integrals at FWHM for the aluminum and silicon peaks were

recorded for each of the 25 particles. The total counts for
aluminum was divided by the total counts for silicon for each
of the 25 particles. Use of the Al/Si ratio eliminates
topographical variations for each point analyzed. The 25
5   Al/Si ratios were then arithmetically averaged to give value
for the average Al/Si ratio at surface and the standard
deviation of these 25 Al/Si ratios was calculated by standard
statistical method. Results are shown in Table 2A.

Cross-section Analysis of Aluminum and Silicon Elemental
10   Distribution
     Prior to gold-coating the disk, the catalyst powder was
sectioned by running a microtome blade across the tape at a
30° angle. An area containing at least 5 cross-sectioned
particles at 500X was selected, imaged, and mapped as in the
15   surface analysis. 5 to 10 particles were randomly chosen
from the picture and labelled from 1 to 10. Aluminum and
silica signal were collected in similar manner as described
in the surface analysis, except that for each particle, the
aluminum and silicon signals were collected at the center of
20   each particle and then at the edge of each particle. The
edge is typically within 2 microns from the outermost
boundary of the silica cross-section. The aluminum and
silicon signals were collected from the 5 to 10 particles.
The total counts for aluminum was divided by the total counts
25   for silicon for all the signals. Use of the Al/Si ratio
eliminates topographical variations for each point analyzed.
The 5 to 10 Al/Si ratios at the center of the silica particle
were then arithmetically averaged to give value for the
average Al/Si ratio at center, and the standard deviation of
30   these 5 to 10 Al/Si ratios at center were calculated by
standard statistical method. Results are shown in Table 2B.
Similarly, calculation were obtained for the average Al/Si
ratio at edge and the standard deviation of these 5 to 10
Al/Si ratios at edge. Results are shown in Table 2C.

2. Results

Table 2A: Surface analysis: Al and Si Signals Measured from 25 Particles

Catalyst Batch Examples	Average Al/Si at Surface	Standard deviation	Standard Deviation as % of Average Al/Si
11	0.34	0.05	15%
12	0.34	0.05	15%
13	0.37	0.05	14%

Table 2B: Cross-section Analysis at Silica Center Al and Si Signals Measured from 5 to 10 Silica Particles

Catalyst Batch Examples	Average Al/Si at center of cross-section	Standard Deviation	Standard Deviation as % of Average Al/Si
11	0.36	0.06	17%
12	0.35	0.06	17%
13	0.34	0.07	21%

Table 2C: Cross-section Analysis at Silica Edge Al and Si Signals Measured from 5 to 10 Silica Particles

Catalyst Batch Examples	Average Al/Si at edge of cross-section	Standard Deviation	Standard Deviation as % of Average Al/Si
11	0.36	0.03	8%
12	0.34	0.06	18%
13	0.33	0.04	12%

The distribution of the Al element is very uniform as shown by the average Al/Si ratios. All the average Al/Si ratios are within the range of 0.33 to 0.37; indicating that the Al distribution is very uniform from one example to another example. It should be noted that as the Al loading on the silica changes this Al/Si ratio would change also.

What is important here is that the ratio is very uniform from sample to sample.

Also by comparing the Al/Si ratio at the surface, at the cross-section center, and at the cross section edge, one
5   observed a range of 0.33 to 0.37 indicating that the Al distribution within each silica particle is very uniform.

FTIR and Solid State NMR Spectroscopy

A spectrum of FTIR and a spectrum of solid state NMR or a catalyst prepared similar to example 11 are attached. These
10   spectra showed that the hydroxyl group on the silica have been reacted with the methyalumoxane and that the methylalumoxane after reaction with the silica no longer has the same solid state NMR signal confirming the chemical change in the methylalumoxane.
15   Catalyst prepared by this method show very uniform distribution of aluminum element (derived from alumoxane) within the silica particles and among the silica particles. The uniform distribution of metals is determined by microscopy techniques and the novel catalyst satisfies the
20   following relationships:

1. The Al/Si ratio at catalyst outer surfaces has a standard deviation is no more than 25% of the average Al/Si ratio at catalyst surfaces.

2. The Al/Si ratio at center of cross-sectioned catalyst
25   particles has standard deviation that is no more than 40% of the average Al/Si ratio at center of cross sectioned catalyst particles.

3. The Al/Si ratio at edge of cross-sectioned catalyst particles has standard deviation that is no more than 40% of
30   the average Al/Si ratio at edge of cross-sectioned catalyst particles.

4. (Average Al/Si surface - Average Al/Si cross section edge)/Average Al/Si surface <25%

5. (Average Al/Si cross section edge - Average Al/Si
35   cross section center)/Average Al/Si cross section edge <30%

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      Catalysts that do not contain Al and Si are excluded, by
the foregoing criteria, and catalyst, that are overloaded
with methylalumoxane would also be excluded due to an
overlayer of Al.

5   During the catalyst preparation, the Al from MAO reacted
with the silica quickly such that less than 1% of the total
Al from MAO was still left in the solvent. Most of the Al
from MAO was anchored in the silica sites, and therefore no
washing step is required.

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CLAIMS:

1.   An olefin polymerization or copolymerization
catalyst, for producing products exhibiting a bulk density of
15 to 36 lb/ft3,
5   wherein the catalyst is in the form of particles,
               wherein said particles have an average particle size
in the range of 1 to 500 microns;
               wherein said particles comprise silica, a transition
metal and aluminum,
10   wherein the molar ratio of aluminum to transition
metal ranges from 70 to 400; wherein said silica is amorphous
and porous and has a pore volume of 0.1 to 3.5 cm3/gm;
wherein said silica has a concentration of silanol groups
wherein the concentration of silanol groups is at least 0.4
15 mmole per gram of silica;
               wherein the silica is contacted with a solution
comprising a source of aluminum which is selected from the
group consisting of an alumoxane, derivatives of alumoxane
and admixtures thereof, and a liquid medium which is
20 effective to disperse the source of aluminum in said
particles whereby each particle exhibits an average Al/Si
ratio (as measured by scanning electron microscopy), wherein
each particle is characterized by (a) an average Al/Si ratio
at the surface of the catalyst particle; (b) an average Al/Si
25 ratio at the center of the catalyst particle; and (c) an
average Al/Si ratio at the edge of the cross section of the
catalyst particle, wherein the difference between any
numerical value of (a), (b), and (c) is less than 30%.

2.   The catalyst of Claim 1, wherein the liquid medium
comprises a straight or branched chain aliphatic or alicyclic
hydrocarbon containing 5 to 20 carbon atoms.

3.   The catalyst of Claim 2, wherein the liquid medium
comprises a solvent for alumoxane.

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4.   The catalyst of Claim 1, wherein said transition
metal is provided by a metallocene which has a formula,
$Cp_mMA_nB_p$, wherein:

   Cp is a cyclopentadienyl or a substituted
5 cyclopentadienyl group;

      m is 1 or 2;

      M is zirconium or hafnium; and

      each of A and B is selected from the group consisting
of a halogen atom, a hydrogen atom and an alkyl group,
10 providing that m+n+p is equal to the valence of the metal M;

      wherein said alumoxane has a formula (a) or (b)

      wherein (a) is $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear
alumoxanes and (b) is $(-Al(R)-O-)_m$ for oligomeric cyclic
alumoxane wherein n is 1-40, m is 3-40, and R comprises a C_1-
15 C_8 alkyl group; wherein said contacted silica is an activated
catalyst.

   5.   The catalyst of Claim 2, wherein the concentration of
silanol groups ranges from greater than .7 up to 2.5
millimoles per gram silica.

   6. The catalyst of Claim 1, wherein said solution
provides an Al:Zr mole ratio of 70 to 400.

   7.   The catalyst of Claim 1, wherein said solution
provides an Al:Zr mole ratio of 100 to 350.

   8.   The catalyst of Claim 4, wherein the aluminoxane is
methylalumoxane.

   9.   The catalyst of Claim 3, wherein the solution
comprises an aromatic hydrocarbon containing 6 to 10 carbon
atoms.

   10.   The catalyst of Claim 2, wherein the solution
comprises a hydrocarbon which contains 5 to 20 carbon atoms.

11. The catalyst of Claim 9, wherein the aromatic hydrocarbon is a halogenated hydrocarbon.

12. The catalyst of Claim 10, wherein the hydrocarbon is aliphatic or alicyclic hydrocarbon and is selected from the group consisting of cyclopentane, cyclohexane, cycloheptane, pentane, isopentane, hexane, isohexane, heptane, octane,
5 nonane, a dodecane and admixtures thereof.

13. The catalyst of claim 4 wherein the metallocene is bis(n-butylcyclopentadienyl) zirconium dichloride; and
     wherein said solution comprises a liquid medium effective to disperse the source of aluminum in said
5 particles whereby each particle exhibits an average Al/Si ratio (as measured by scanning electron microscopy), wherein each particle is characterized by (a) an average Al/Si ratio at the surface of the catalyst particle; (b) an average Al/Si ratio at the center of the catalyst particle; and (c) an
10 average Al/Si ratio at the edge of the cross section of the catalyst particle, wherein the difference between any numerical value of (a), (b), and (c) is less than 15%.

14. The catalyst of Claim 13, wherein aluminoxane is chemically reacted onto a surface of the silica.

15 15. A method for preparing a supported metallocene catalyst which comprises:
     a) dissolving a metallocene in a solution of alumoxane;
     b) adding the solution to a silica,
        wherein the silica contains active hydrogen for
20 reaction with methylalumoxane and is slurried in a hydrocarbon liquid or a mixture of hydrocarbon liquids;

c) allowing the methylalumoxane and metallocene to react
with the silica such that more than 99% of the
methylalumoxane and 99% of the metallocene are impregnated
onto a surface of the silica; and

5   d) recovering a free flowing catalyst powder.

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

IPC(6)   :B01J 31/26, 31/32
US CL   :502/104, 117, 120, 152

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

  U.S. :   502/104, 117, 120, 152

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,206,199 A (KIOKA et al.) 27 April 1993, see columns 17 and 18.	1-15
Y	US 5,332,706 A (NOWLIN et al.) 26 July 1994, see column 7.	1-15

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed

"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 AUGUST 1997	0 1 OCT 1997

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